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⑤4硫化亜鉛系薄膜の製造方法

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明　細　書

1、発明の名称

硫化亜鉛系薄膜の製造方法

2、特許請求の範囲

(1)　硫化亜鉛を主成分とし、アルカリ金属、またはアルカリ土類金属の内から少なくとも一種類以上を含有する硫化亜鉛系焼結体に電子ビームを照射し、前記硫化亜鉛系焼結体を加熱蒸発させ、基板上に硫化亜鉛系薄膜を堆積させることを特徴とする硫化亜鉛系薄膜の製造方法。

(2)　前記硫化亜鉛系焼結体が、Mn，Cu，Ag，Al，Tb，Dy，Er，Pr，Sm，Ho，Tm、またはこれらのハロゲン化物のうち少なくとも1種類以上を含むことを特徴とする特許請求の範囲第1項に記載の硫化亜鉛系薄膜の製造方法。

(3)　前記アルカリ金属が、Li，Na，K，Rb，Csより成ることを特徴とする特許請求の範囲第1項に記載の硫化亜鉛系薄膜の製造方法。

(4)　前記アルカリ金属の亜鉛に対する濃度が0.1～2原子%であることを特徴とする特許請求の範囲第1項に記載の硫化亜鉛系薄膜の製造方法。

(5)　前記アルカリ土類金属が、Ca，Mg，Sr，Baより成ることを特徴とする特許請求の範囲第1項記載の硫化亜鉛系薄膜の製造方法。

(6)　前記アルカリ土類金属の亜鉛に対する濃度が、特許請求の範囲第1項に記載の0.02～2原子%であることを特徴とする硫化亜鉛系薄膜の製造方法。

3、発明の詳細な説明

本発明は、硫化亜鉛系薄膜の製造方法に関し、とりわけ、薄膜中に微小粒子や、ピンホールを含まない均質で高品質な硫化亜鉛系薄膜の製造方法に関するものである。

従来、硫化亜鉛系薄膜は、硫化亜鉛系焼結体を電子ビーム蒸着することにより形成されていた。この際用いる硫化亜鉛系焼結体は、硫化亜鉛粉末またはMn，Cu，TbF_3などの活性物質を含む硫化亜鉛粉末を、たとえば400㎏の圧力で成形し、不活性ガスまたは硫化水素を含む不活性ガス中で、1000℃～1200℃の温度で、1～3時間焼成することにより形成されていた。このように形成

した硫化亜鉛系焼結体に電子ビームを照射し、加熱蒸発させ、硫化亜鉛系薄膜を形成した場合、薄膜中に１～２０ミクロンの粒径の微小粒子やピンホールが生ずるという欠点があった。またこのような薄膜をＥＬ薄膜として応用した場合、微小粒子やピンホールが原因となり、絶縁破壊を引き起し、安定なＥＬ素子を形成することができない。

このように薄膜中に微小粒子やピンホールを生ずる原因は、従来の方法で作成した硫化亜鉛系焼結体が理論密度の８０～７５％程度の密度しかなく、また硫化亜鉛系焼結体は高温で昇華蒸発するため、電子ビームを照射したとき、硫化亜鉛系焼結体が帯電し、静電的反発力により微小粒子が飛散し、基板表面に付着するためと考えられる。

本発明は上記従来技術にもとづき硫化亜鉛を主成分とする粉末に、アルカリ金属またはアルカリ土類金属を添加して、不活性ガスまたは硫化雰囲気中で熱処理することにより形成した硫化亜鉛系焼結体に電子ビームを照射し、加熱蒸発させる、いわゆる電子ビーム蒸着を行ない薄膜中の微小粒子やピンホールが皆無に近い高品質で均質な硫化亜鉛系薄膜が形成するものである。

このような方法で作成した硫化亜鉛系焼結体は、密度が高く、粒径が大きいため、電子ビームを照射した場合、昇華が焼結体表面から一様に起るため上記特性を得られると考えられる。また添加するアルカリ金属としては、Li，Na，K，Rb，Csが有効であり、添加量としては 亜鉛に対する濃度が0.1～２原子％が適当であった。つまり、0.1％以下では効果が微弱であり、２％以上では焼成時にボートと反応する欠点があった。アルカリ土類金属としては、Ca，Mg，Sr，Ba が有効であり、添加量としては、亜鉛に対する濃度が0.02～２原子％が適当であった。つまり0.02原子％以下では効果が微弱であり、２原子％より上では焼成時にボートと反応する欠点があった。また硫化亜鉛系焼結体中に、Mn，Cu，Ag，Al，Tb，Dy，Er，Pr，Sm，Ho，Tm またはこれらのハロゲン化物のうち少なくとも１種類以上を含む場合においても、アルカリ金属またはアルカリ土類金属の添加が有効である。

以下実施例により説明する。市販の硫化亜鉛粉末（粒径0.1～1.5ミクロン）に、種々のアルカリ金属化合物やアルカリ土類金属化合物を添加し、乳鉢により混合した後、約１０重量％の水を加え、さらに混合した後造粒した。この粉末を４００㎏の圧力で成形し、直径１５㎜、厚さ１０㎜の円柱体とし、これを硫化雰囲気または不活性ガス雰囲気中で、１０００～１２００℃の温度で、１時間の焼成を行なった。第１表に、使用したアルカリ金属化合物またはアルカリ土類金属化合物の種類および濃度、焼成雰囲気、焼成温度、焼成時間、および得られた硫化亜鉛系焼結体の密度（理論密度に対する割合）を示す。

表から判るように得られた焼結体の密度は、理論密度の９０％以上であった。この焼結体を用いて、電子ビーム蒸着により硫化亜鉛系薄膜を形成したところ、従来の製法の硫化亜鉛系焼結体を用いて同様に形成した薄膜に比べて、薄膜中の微小粒子やピンホールの数が激減し、高品質で均質な硫化亜鉛系薄膜を形成することができた。

また図面に示すようなＥＬ素子のＥＬ発光体層４を0.03原子％の塩化バリウムを含む硫化亜鉛系焼結体を電子ビーム蒸着し、同時に抵抗加熱によりMnを蒸着し、0.8原子％のMnを含む硫化亜鉛薄膜で形成し、発光特性を測定した結果、微小な絶縁破壊も極めて少なく、安定なＥＬ素子であることが判明した。

以　下　余　白

表

添加物質		焼成条件			密度
種類	濃度(原子%)	雰囲気	温度(℃)	時間(hr)	(%)
LiCl	2	H_2S	1000	1	91
$LiNO_3$	2	H_2S	1000	1	91
NaCl	2	H_2S	1000	1	91
KCl	2	H_2S	1100	1	90
RbCl	2	H_2S	1100	1	90
CsCl	2	H_2S	1100	1	90
$BaCl_2$	0.3	Ar	1100	1	98
$BaCl_2$	0.03	H_2S	1100	1	91
$BaCl_2$ $SrCl_2$	0.1 0.1	H_2S	1200	1	98
$BaCl_2$ $CaCl_2$	0.1 0.1	H_2S	1200	1	98
$BaCl_2$ $MgCl_2$	0.1 0.1	H_2S	1200	1	98
$Ba(OH)_2$	0.1	H_2S	1100	1	96

以上のように、本発明の製法によれば、ピンホールや微小付着物が極めて少なく良質の硫化亜鉛系薄膜が再現性よく形成でき、光学薄膜，螢光体薄膜，ＥＬ薄膜として応用した場合、光学特性や安定性の優れた素子を形成することができる。

4、図面の簡単な説明

図面は、本発明の一実施例の製造方法により形成されたＥＬ素子の構造を示す図である。

１……ガラス基板、２……透明電極、３……酸化イットリウム薄膜、４……マンガン付活硫化亜鉛薄膜、５……酸化イットリウム薄膜、６……アルミニウム電極。

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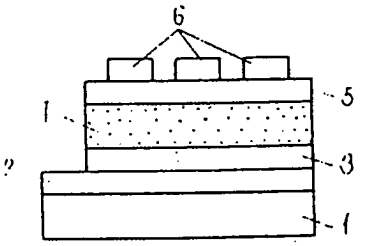

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(54) Manufacturing method of zinc sulfide thin film

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Details
1. Name of invention
Manufacturing method of zinc sulfide thin film

2. Range of the patent claims
(1) It is a manufacturing method of the zinc sulfide related thin film, which shall be characterized by piling the zinc sulfide related thin film on the substrate by irradiating electron beam to zinc sulfide related sintered body and heating to make the abovementioned zinc sulfide related sintered body to be evaporated, which shall contain the main ingredient as zinc sulfide and at least one kind of the alkaline metals or the alkaline earth metals.
(2) It is a manufacturing method of the zinc sulfide related thin film, which is mentioned in Claim 1 of the range of the patent claims, which shall be characterized by containing at least one kind of the halogen converted materials, which are Mn, Cu, Ag, Al, Tb, Dy, Er, Pr, Sm, Ho and Tm as the abovementioned zinc sulfide related sintered body.
(3) It is a manufacturing method of the zinc sulfide related thin film, which is mentioned in Claim 1 of the range of the patent claims, which shall be characterized by being composed of Li, Na, K, Rb and Cs as the abovementioned alkaline metals.
(4) It is a manufacturing method of the zinc sulfide related thin film, which is mentioned in Claim 1 of the range of the patent claims, which shall be characterized by having the amount of density against the abovementioned alkaline metals to be between 0.1 and 2 atm%.
(5) It is a manufacturing method of the zinc sulfide related thin film, which is mentioned in Claim 1 of the range of the patent claims, which shall be characterized by being composed of Ca, Mg, Sr and Ba as the abovementioned alkaline earth metals.
(6) It is a manufacturing method of the zinc sulfide related thin film, which is mentioned in Claim 1 of the range of the patent claims, which shall be characterized by having the density against zinc of the abovementioned alkaline earth related metals, which is in between 0.02 to 2 atm%.

3. Detailed explanation of the invention
This invention is concerning the manufacturing method of the zinc sulfide thin film, especially it is concerning the manufacturing method of the high quality zinc sulfide thin film, which does not have small particles nor pin holes within the thin film.

Currently, the zinc sulfide thin film is created by applying the electron beam deposition to the zinc sulfide sintered body. The zinc sulfide sintered body which is used in this case is created by firing for one to three hours at the temperature of between 1000 °C and 1200 °C within the inert gas or the inert gas which shall contain hydrogen sulfide after

molding zinc sulfide powder or zinc sulfide powder which shall contain the active substance such as Mn, Cu or TbF_3, etc. at the pressure of 400 kg / cm^2. In the case that the zinc sulfide thin film is created by the zinc sulfide sintered body, which the electron beam is irradiated to and shall be evaporated by heating, there was a problem of generating small particles of the particle sizes of 1 to 20 micron and pin holes within the thin films. Also, when applying such thin films as for the EL thin film, because of the small particles and pin holes, insulation destruction shall occur, and as a result, it is not possible to create a stable EL element.

The cause of generating small particles and pin holes is because the zinc sulfide sintered body, which is created by the existing method, shall only have the density of 60 to 75% of the theoretical density, and also because the zinc sulfide sintered body shall evaporate by sublimation, the zinc sulfide sintered body is charged when the electron beam is irradiated, and small particles are scattered by the electrostatic repulsion, then they would be stuck to the surface of the substrate.

This invention shall create the zinc sulfide thin film, which shall have high quality and shall have almost no pin holes within the thin films by performing the electron beam deposition technique, which is to irradiate the electron beam to the zinc sulfide sintered body, which is created by giving the treatment within the inert gas atmosphere or sulfide atmosphere by adding alkaline metals or alkaline earth metals to the powder, which shall have zinc sulfide as the main material, based on the abovementioned existing technique.

It is probably because when creating the zinc sulfide sintered body using such a method, the density would be high and the particle size would be large, therefore, by making it as the target, sputtering shall occur from the surface of the sintered body at the even composition and equally to the whole surface. Also, as for the adding alkaline metals, Li, Na, K, Rb or Cs are effective, and as for the additional amount, 0.1 atom% to 2 atom% of the thickness against zinc was the suitable amount. Therefore, if it is less than 0.1%, the effect would be very weak, and if it is more than 2%, it would react against the firing container when firing.

As for the alkaline earth metals, Ca, Mg, Sr and Ba are effective, and as to the addition amount, 0.02 atom% to 2 atom% of the thickness against zinc was the suitable amount. Therefore, if it is less than 0.02 atom%, the effect would be very weak, and if it is more than 2 atom%, it would react against the firing container when firing. Also, in the case that at least one of the halide of Mn, Cu, Ag, Al, Tb, Dy, Er, Pr, Sm, Ho or Tm is contained, the addition of the alkaline metal or the alkaline earth metal would also be effective.

Hereinbelow, an explanation shall be made according to the implementation example. Various alkaline metallic compounds or various alkaline earth metallic compounds are added to the zinc sulfide powder (particle size 0.1 to 1.5 micron, goods on the market), and after mixing shall be performed by a mortar, approximately 10 weight% of water shall be added, and mixed together again, then granulated. This powder was molded at the pressure of 400 kg/cm^2 in order to create a cylinder of the diameter 15 cm and the

thickness 10 mm, then firing was performed to this within the inert gas atmosphere at the temperature of between 1000 and 1200 °C for one hour. This table shall indicate the type, firing atmosphere, firing temperature and firing period of alkaline metallic compound or alkaline earth metallic compound used as well as the density of the zinc sulfide sintered body which was obtained (rate against theoretical density).

As it is seen from the table, the density of the sintered body, which was obtained, was more than 90% of the theoretical density. Using this sintered body, zinc sulfide thin film was created by the electron beam deposition technique. The result was that it was able to create the zinc sulfide thin film of higher quality and good crystallization compared to the thin film, which is created by the zinc sulfide sintered body and powder style, which are made by the existing manufacturing method, and it had almost no small particles and pin holes within the thin film.

Also, it was discovered that the stable EL element, which shall have only extremely small insulation destruction, can be obtained from the result of measuring the emitting characteristics of material, which is the EL emitting layer of the EL element, which is shown in the figure, is created by giving the electron beam deposition to the zinc sulfide sintered body, which shall contain barium chloride of 0.03 atom%, and also the deposition is applied to Mn by the resistance heating, and then the zinc sulfide, which shall contain 0.8 atom % of Mn, is created.

As it is mentioned, by using the manufacturing method of this invention, high quality zinc sulfide thin film which produces extremely small numbers of pin holes and small particles can be created with a good reproduction, and when it is applied to the use of the optical thin film, the phosphor thin film and the EL thin film, it is able to create the element with excellent stability and optical characteristics.

4. Simple explanation of the figure

The figure shows the structure of the EL element, which is created by the manufacturing method of the implementation example of this invention.

1. Glass substrate
2. Transparent electrode
3. Yttrium oxide thin film
4. Manganese added zinc sulfide thin film
5. Yttrium oxide thin film
6. Aluminum electrode

Name of Attorney: Patent attorney Toshio Nakao (and one more person)

Table

Addition substance		Firing condition			Density (%)
Type	Thickness (atom%)	Atmosphere	Temperature (°C)	Time (hour)	
LiCl	2	H_2S	1000	1	91
$LiNO_3$	2	H_2S	1000	1	91
NaCl	2	H_2S	1000	1	91
K Cl	2	H_2S	1100	1	90
RbCl	2	H_2S	1100	1	90
CsCl	2	H_2S	1100	1	90
$BaCl_2$	0.3	Ar	1100	1	98
$BaCl_2$	0.03	H_2S	1100	1	91
$BaCl_2$ $SrCl_2$	0.1 0.1	H_2S	1200	1	98
$BaCl_2$ $CaCl_2$	0.1 0.1	H_2S	1200	1	98
$BaCl_2$ $MgCl_2$	0.1 0.1	H_2S	1200	1	98
$Ba(OH)_2$	0.1	H_2S	1100	1	95